Supporting Information

Quantum Mechanics Reactive Dynamics Study of Solid Li-Electrode/Li_6PS_5Cl-Electrolyte Interface

Tao Cheng,[†] Boris V. Merinov,[†] Sergey Morozov,[‡] and William A. Goddard III[†]*

[†]Materials and Process Simulation Center, MC 139-74, California Institute of Technology, Pasadena, California 91125, United States

[‡]South Ural State University, 76 Lenin Ave., Chelyabinsk, Russia 454080, Russia

Simulation Methods

The electronic structure calculations were performed using the DFT method implemented in the Vienna ab initio simulation package (VASP),[1-4] a plane wave electronic structure code. The exchange and correlation energies were calculated using the Perdew, Burke, and Ernzerhof (PBE) functional within the generalized gradient approximation (GGA)[5-6] and the projector augmented wave (PAW) method.[7] Spin polarization did not have an appreciable effect on the overall energies. Therefore, the calculations were carried out without spin polarization to reduce the computational demands.

We used a plane-wave cutoff energy of 400 eV and the first order Methfessel-Paxton scheme with a smearing width of 0.2 eV. Dipole corrections were applied along the z direction of the system (see Figure 4). The energy minimization criterion was < 0.02 eV/Å for all forces on free atoms. The charges on various species were derived using a Bader analysis.[8]

A 1.2 fs time step was applied in our Ab Initio Molecular Dynamics (AIMD) simulations. Only the gamma point of the Brillouin zone with no consideration of symmetry was sampled in the AIMD computations. The velocities were rescaled every 20 MD steps to readjust the target temperature to equilibrium. A Nose-Hoover thermostat was employed for the NVT AIMD simulations.

References

(1) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993,** *47*, 558-561.

(2) Kresse, G.; Hafner, J. Ab Initio Molecular-Dynamics Simulation of the Liquid-Meta Amorphous-Semiconductor Transition in Germanium. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994,** *49*, 14251-14269.

(3) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996,** *6*, 15-50.

(4) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996,** *54*, 11169-11186.

(5) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Atoms, Molecules, Solids, and Surfaces: Applications of the Generalized Gradient Approximation for Exchange and Correlation. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992,** *46*, 6671-6687.

(6) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Erratum: Atoms, Molecules, Solids, and Surfaces: Applications of the Generalized Gradient Approximation for Exchange and Correlation. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993,** *48*, 4978-4978.

(7) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999,** *59*, 1758-1775.

(8) Henkelman, G.; Arnaldsson, A.; Jónsson, H. A Fast and Robust Algorithm for Bader Decomposition of Charge Density. *Comput. Mater. Sci.* **2006,** *36*, 354-360.